THERMOELECTRIC PHENOMENA IN MEMBRANE STRUCTURES

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The influence of temperature gradients on electric membrane potentials and processes of ion transport in cell structures is studied with the thermodiffusion effects taken into account. The thermodiffusion distribution of ion concentration in a system with membranes is found. The shifts of ion concentration under the influence of temperature gradients are examined. They have an exponential shape with respect to the product of Soret coefficient and temperature difference.

The dependence of electric membrane potentials and processes of passive ion transport on the thermodiffusion characteristics, the temperature and concentration gradients is analysed. Numerical values of the thermodiffusion properties in thermoelectric membrane phenomena are obtained. The proposed results are of importance with taking into account the influence of external temperature fields on bioobjects under the application of hyper- and hypothermia in modern medical practice.

Keywords: membrane cell potential, temperature gradient, thermodiffusion, Soret coefficient.

Introduction

Dependence of membrane cell potentials on the concentration of various inorganic ions is described by a theory which is valid for the case of thermodynamic equilibrium. Main results of this theory are based on the assumption that the temperature, pressure and chemical potentials are equal for both sides of membranes and the gradients of concentration ∇C and electric potential $\nabla \varphi$ exist. The flow of charged particles is properly described by the well-known electrodiffusion Nernst-Plank equation (see, for example, [1-3]).

Isothermal conditions are violated while the medical methods of hyper- and hypothermia are used. The influence of temperature gradients ∇T on the membrane cell potentials could be taken into account by linear laws of the thermodynamics of irreversible processes. The main idea consists in generalization of the Nernst-Plank equation for the case of temperature gradients and in deriving expression for the thermoelectrochemical potential which gradient is a moving force for ion flow through membrane structures with non-zero gradients of concentration, electric field potential and temperature. A formula for the Nernst concentration potential can be derived from the condition that the thermoelectrochemical potentials are equal for both sides of membranes and with temperature gradients taken into account.

The solution of the generalized Nernst-Plank equation gives us an expression for the ion flow through membrane under the action of gradients ∇C, $\nabla \varphi$ and ∇T. Taking this equation into account and consider only univalent ions K^+, Na^+ and Cl^-, it is possible to get an expression for the stationary membrane Goldman-Hodgkin-Katz potential under non-isothermal conditions.

Thus, such formulae will give us the dependence of membrane cell potentials on the ion concentrations, temperature gradients and thermodiffusion properties like the Soret coefficient. Experimental data for this coefficient allow us to evaluate numerical values of non-isothermal membrane cell potentials.

Thermodiffusion Distribution of Ion Concentration

Thermodiffusion distribution of ion concentration in a system with membranes was studied in [4] with peculiarities of passive and active transport taking into account. The dependence of shifts of ion concentration for both sides of membranes on the temperature gradient was obtained from the condition of stationary flow through membranes for each sort of ions. Respectively, one has for ions K^+

$$(\Delta C)_K = ([K]_i - [K]_e) \frac{e^{\sigma_K \Delta T} - 1}{e^{\sigma_K \Delta T} + 1} \tag{1}$$

and for ions Na^+

$$(\Delta C)_{Na} = ([Na]_i - [Na]_e) \frac{e^{\sigma_{Na} \Delta T} - 1}{e^{\sigma_{Na} \Delta T} + 1}. \tag{2}$$

Here $(\Delta C)_K$ and $(\Delta C)_{Na}$ are the shifts of ion concentrations for both sides of membranes (at approximation of symmetrical distribution); $[K]_i$, $[Na]_i$ are the ion

concentrations inside a cell for zero temperature gradient; $[K]_e$, $[Na]_e$ are the concentrations of these ions outside for zero temperature gradient; $\Delta T = T_e - T_i$ is the difference of temperature outside and inside a cell; σ_K, σ_{Na} are the Soret coefficients for ions K^+ and Na^+.

Figures 1 and 2 show graphical dependence of thermodiffusion shifts of ion concentrations $(\Delta C)_K$ and $(\Delta C)_{Na}$ for the gigantic calmar's axone where the ion concentrations are respectively as follows: $[K]_i = 392$ mM/l, $[Na]_i = 78$ mM/l and $[K]_e = 22$ mM/l, $[Na]_e = 462$ mM/l [2]. Values of σ_K, σ_{Na} can be taken from experiments on thermodiffusion in electrolyte solutions [5, 6]: $\sigma_K = 1.18 \cdot 10^{-3}$ K^{-1}, $\sigma_{Na} = 2 \cdot 10^{-3}$ K^{-1}.
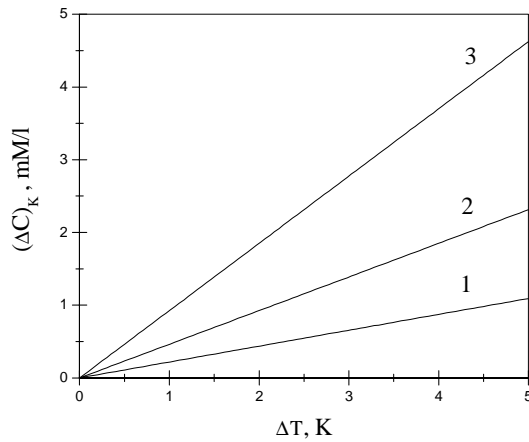
Fig. 1. Dependence of the thermodiffusion shift of ion concentration for K^+ on temperature difference under various values of σ_K: $1.18 \cdot 10^{-3}$, $2.5 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ K^{-1}.
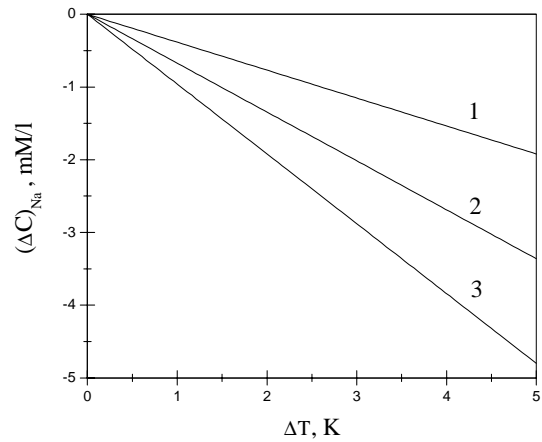
Fig. 2. Dependence of the thermodiffusion shift of ion concentration for Na^+ on temperature difference under various values of σ_{Na}: $2 \cdot 10^{-3}$, $3.5 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ K^{-1}.

In cases of aqueous electrolyte solutions with thermodiffusion the concentration of dissolved electrolyte always increases in cold region, this fact being confirmed by numerous experiments [5-7]. We consider, for certain condition, such a situation that $T_e > T_i$, i.e. $\Delta T > 0$. As is seen from Fig.1 and Fig.2, for this case $(\Delta C)_K > 0$, $(\Delta C)_{Na} < 0$. A physical explanation of this result connects with higher temperature of the external surroundings and, respectively, the thermodiffusion ion flow occurs because of a higher kinetic energy of ions. In the case of K^+ ions this flow supports a flow of K^+ ions under its active transport. For Na^+ ions the situation is quite opposite: the thermodiffusion flow of Na^+ ions has an opposite direction with respect to a flow of Na^+ ions under its active transport.

The Concentration Nernst Potential

Using general notions of the thermodynamics of irreversible processes, it is possible to write the following expression for the flow of charged particles (ions) through membranes with gradients ∇C, $\nabla \varphi$ and ∇T taking into account:

$$\vec{I} = -D\vec{\nabla}C - Cb\vec{\nabla}\varphi - DC\sigma\vec{\nabla}T. \tag{3}$$

Eq. (3) gives a generalized Nernst-Plank equation for the case of non-zero temperature gradient. Here I is the density of flow in moles per unit square and unit time; C is the ion concentration in moles per unit volume; φ is the potential of electric field; T is the absolute temperature; D, b, σ are the coefficients of diffusion, mobility and Soret for a fixed sort of ions.

Let us transform this equation to the Teorell equation (see, for example, [3]). For this purpose, first we take out a factor $(-Cb/zF)$ together with a gradient operator and receive

$$\vec{I} = -\frac{Cb}{zF}\vec{\nabla}\left(\mu_0 + zF\varphi + \frac{zFD}{b}\ln C + \frac{zFD}{b}\sigma T\right). \tag{4}$$

Here z is the valency, F is the Faraday constant. The quantity in brackets is naturally called the thermoelectrochemical potential gradient of which being a moving force for ion flow in this case.

The condition of ion equilibrium is equality of thermoelectrochemical potentials for both sides of membrane. It gives a generalized expression for the Nernst concentration potential with temperature gradients taking into account

$$\varphi_M = \frac{RT_a}{zF}\left\{\ln\frac{C_i}{C_e} + \sigma(T_i - T_e)\right\}. \tag{5}$$

Here T_a is the average temperature in a system. It is necessary to mention that the concentrations in eq. (5) must be calculated in accordance with formulae (1) and (2).

Non-Isothermal Stationary Membrane Potential

Solution of eq. (3) can be written in the following form using the approximation of constant gradients of electric potential and temperature (this approximation is valid for membranes of small thickness, including biomembranes):

$$I = \tilde{\psi}P\frac{C_e\exp\tilde{\psi} - C_i}{1 - \exp\tilde{\psi}}. \tag{6}$$

Here P is the coefficient of permeability for a fixed sort of ions and

$$\tilde{\psi} = \frac{b}{D}(\varphi_e - \varphi_i) + \sigma\Delta T \tag{7}$$

is the generalized dimensionless membrane potential.

With allowance for eq.(6) written for univalent ions K^+, Na^+, Cl^- and taking into account the stationary condition for the whole flow (see, for example, [2-3]), one has the following formula for the stationary membrane potential with non-zero temperature gradient:

$$\varphi_{stat} = \varphi_{stat}^{0} + \Delta\varphi. \tag{8}$$

Here φ_{stat}^{0} is the term given by a well-known expression by Goldman, Hodgkin, Katz and $\Delta\varphi$ is the additional term appeared due to the temperature gradient

$$\Delta\varphi = \frac{RT_a}{2F}\left\{\gamma\Delta n\left(\Delta C_j, P_j\right) + \eta\left(\Delta C_j, P_j, \sigma_j\right)\Delta T\right\} \tag{9}$$

where γ is the function depends on initial ion concentrations, Δn and η are the functions depend on initial ion concentrations and values ΔC for each sort of ions (explicit forms of these functions are known and do not presented here because of its complexity). In accordance with eqs. (1) and (2), the functions Δn and η have only exponential dependences on the product $\sigma\Delta T$. Linear dependence of the membrane potential on ΔT is caused by the second term in eq. (9) and also by the coefficient $(T_i+T_e)/2$ which defines the average temperature of a system.

It is possible to show on principle that taking into account only one sort of ions, say K^+ ions, can simplify eq.(8) and it gives us the concentration non-isothermal Nernst potential (see eq.(5)). Last formula, in its turn, transforms to a well-known expression for the equilibrium concentration Nernst potential (see, for example, [8]).
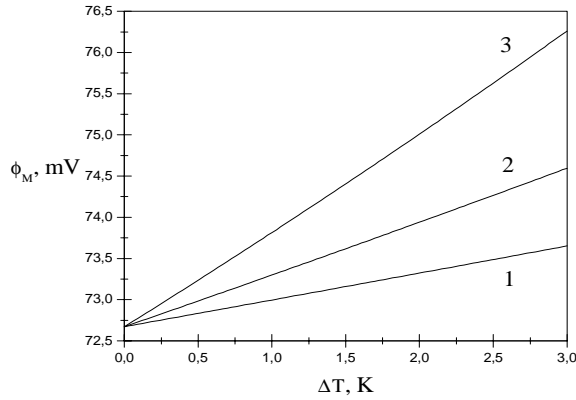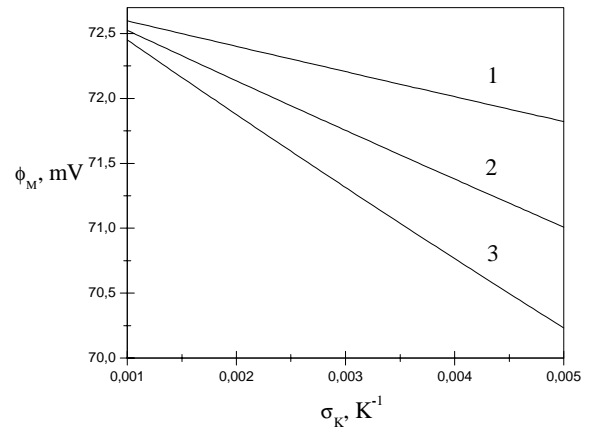

Fig. 3. Dependence of the membrane rest potential on temperature difference $\Delta T=T_e-T_i$ ($\Delta T>0$) under various values of σ_K: $1\cdot10^{-3}$, $2.5\cdot10^{-3}$, $5\cdot10^{-3}$ K^{-1}.
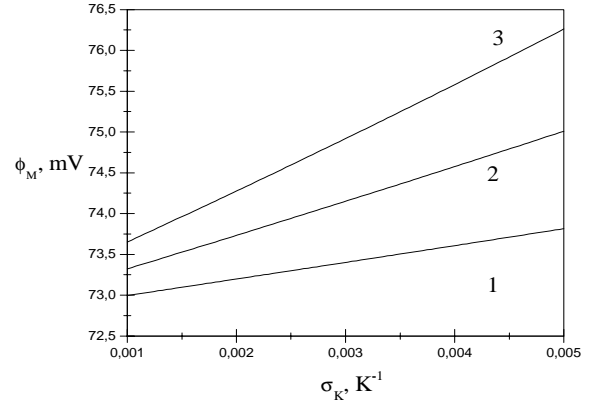
Fig. 4. Dependence of the membrane rest potential on Soret coefficient for K^+ under various values of $\Delta T=T_e-T_i$ ($\Delta T>0$): 1, 2, 3 K.
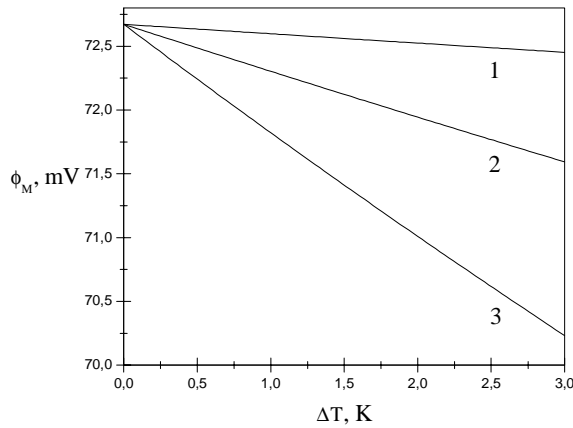
Fig. 5. Dependence of the membrane rest potential on temperature difference $\Delta T = T_i - T_e$ ($\Delta T > 0$) under various values of σ_K: $1 \cdot 10^{-3}$, $2.5 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ K^{-1}.

Fig. 6. Dependence of the membrane rest potential on Soret coefficient for K^+ under various values of $\Delta T = T_i - T_e$ ($\Delta T > 0$): 1, 2, 3 K.

Figures 3–6 show graphical dependence of membrane rest potential on the Soret coefficient for K^+ ions and the temperature difference for both sides of membrane in the calmar's axone. As is seen from these figures, the dependence of the membrane potential is almost linear for concerned intervals. It is obvious that the dependence of φ_M on σ or ΔT has a linear shape for $\sigma \Delta T << 1$ when all exponential functions can be expended in series with linear terms taking into account.

Conclusion

Increase (decrease) of membrane potential has to be observed under increase (decrease) of temperature in the external side of membrane compared with internal temperature, i.e. the internal cell environment becomes more electronegative (electropositive) with respect to external media.

Dependence of membrane potentials on the product $\sigma \Delta T$ is approximately linear within intervals $\Delta T = (0 \div 3)$ K and $\sigma = (1 \cdot 10^{-3} \div 5 \cdot 10^{-3})$ K^{-1}; change of membrane potential approaches 5% of its value for zero temperature gradients. For $\sigma = 1 \cdot 10^{-3}$ K^{-1} and $\Delta T \sim 10^{-1}$ K the change of membrane cell potential is about 10^{-2} mV, this value can be easily registered by modern technique.

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